148. *The Cationic Polymerization of Styrene. Part III.*[1] *The Cocatalytic Action of Water in the Polymerization of Styrene by Aluminium Chloride.*

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By using very carefully dried styrene and pure aluminium chloride, it has been shown that water is necessary for the polymerization.

THE observation by Jordan and Mathieson[2] that styrene is polymerized by aluminium chloride in carbon tetrachloride solution in the absence of a cocatalyst is at variance with the proton-addition theory of Polanyi *et al.*[3] which has been found to hold for several other metal halide catalyst systems. Jordan and Mathieson claimed that the system was anhydrous, and hence that initiation occurred through a π-complex between the olefin and aluminium chloride. This system has been re-investigated under conditions designed to give more stringent drying than previously obtained in order to eliminate the possible cocatalytic action of traces of water.

Experimental.—Materials. A commercial sample of styrene was redistilled and kept over sodium wire which was frequently crushed to expose fresh surfaces. It was then distilled three times *in vacuo*, only the middle third being taken each time, before finally being distilled on to outgassed barium oxide and stored for two weeks.

Aluminium chloride was prepared by Wallace and Willard's method,[4] using pure aluminium turnings and silver chloride made from " AnalaR " reagents. This was sublimed without residue into breakable phials as a white crystalline material.

Apparatus and procedure. A vacuum-line similar to that of Brackman and Plesch[5] was used. After being pumped out with frequent flamings for several days at a pressure less than 10^{-3} mm. the system was shut off from the line, the aluminium chloride phial broken, and styrene distilled from barium oxide on to the aluminium chloride, a cold trap being used. On melting, the styrene was observed to run over the white aluminium chloride with no polymerization and the formation of a very pale straw colour. The styrene could be distilled off, leaving no trace of polymer. On admission of water vapour a bright orange colour developed at the aluminium chloride–styrene interface and polymerization occurred. Larger quantities of water discharged the colour.

Discussion.—These results are in agreement with some otherwise inconclusive kinetic results[6] on the system styrene–aluminium chloride–carbon tetrachloride in which the drying of reagents, although not sufficient to stop polymerization, showed that the polymerization rate was below that obtained by Jordan and Mathieson.[2] The orange colour on addition of water is due to the formation of the 1-phenylethyl ion and the growing polymer ion.[1] It is clear that polymerization must be initiated by proton addition to the styrene and hence water is a cocatalyst. Excess of water discharges the colour because of the known reactivity of carbonium ions.

The system aluminium chloride–styrene–carbon tetrachloride is now in conformity with other polymerizations catalysed by metal halides, since in all systems studied up to the present, the presence of a cocatalyst is essential for reaction to proceed.

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[1] Part II, preceding paper.
[2] Jordan and Mathieson, *J.*, 1952, 611, 621.
[3] Polanyi, Evans, Holden, Plesch, Skinner, and Weinberger, *Nature*, 1946, **157**, 102.
[4] Wallace and Willard, *J. Amer. Chem. Soc.*, 1950, **72**, 5275.
[5] Brackman and Plesch, *J.*, 1953, 1289.
[6] Treloar, Thesis, University of Adelaide, 1958.